

Calculation of the Geometrical Structure of Some AH_n Molecules

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Approximate Hartree-Fock calculations for H_3 , CH_2 , NH_2 , H_2O , H_2O^+ , BH_4^- , NH_4^+ , and CH_4 have been used to determine equilibrium angles and internuclear separations. The results are in good agreement with the experimental values where these exist.

Data from these calculations are used to test the usefulness of a partition into one-electron type terms. It is found that the partitioned energies reflect the influence of the other orbitals in such a way as to render a simple interpretation very difficult. For example, the present results predict an equilibrium angle of 119° for H_2O^+ which is very unexpected if the usual picture of a nonbonding b_1 orbital is accepted.

1. Introduction

Perhaps the most widely used scheme for the prediction of molecular shapes is the correlation diagrams proposed by Walsh [1].¹ The simplicity and popularity of the scheme rests on the assumption that the total energy of the molecule is simply the sum of one-electron orbital energies. Substantially, this is equivalent to an extended Hückel calculation as it is usually applied [2]. Hoffmann notes that such a procedure can be valid only if there is a slow variation with distance for the difference between the nuclear-nuclear repulsion and the electron-electron repulsions.

Reliance upon such a fortuitous cancellation or semiempirical parameterization of the problem is not satisfying in two essential respects. In the first place, as noted by Coulson and Neilson [3], there are fundamental theoretical objections to any one-electron model. Secondly, the predictions of the scheme must be treated more cautiously when applied to changes in molecular geometry attendant upon excitation or ionization.

Coulson and Neilson proposed that the apparent simplicity of the partition of the total energy into one-electron terms be retained, nonetheless, for its obvious pedagogic and predictive value. The partition which they devolved upon is a natural one based on the Hartree-Fock molecular orbital approach. The total energy in the Hartree-Fock approximation can be written, for a closed-shell molecule, as

$$E = \sum_i e_i + V_N, \quad (1)$$

¹ Figures in brackets indicate the literature references at the end of this paper.

where $e_i = E_i + E_i$. V_N is the total nuclear-nuclear repulsion energy, E_i is the expectation value for molecular orbital i of all one-electron potential and kinetic energy operators, and ϵ_i is the i th eigenvalue of the solution of the self-consistent field equations which determine the Hartree-Fock function.

In general, with the exception of V_N , these quantities cannot be determined accurately for a general range of molecular cases. The usual method is to expand the Hartree-Fock orbitals as a linear combination of atomic orbitals. Solution of the resultant equations is by an iterative self-consistent field (SCF) procedure [4]. Accuracy of the variational solutions is predicated upon the number and type of basis functions. The total energy of the system is determined by the SCF program precisely by eq (1) or its analog suitably modified for the open-shell case.

Implicit in this approach is the assumption that the geometry of a molecule can be calculated, to a high degree of accuracy, by a self-consistent field one-electron theory which ignores certain types of correlation. This assumption is buttressed by both experimental numerical work with diatomic molecules [5] and theoretical arguments [6].

However, calculations of polyatomic molecules have not been quite as successful. Much of this difficulty probably can be attributed to the approximate integrals that were used in evaluating the necessary matrix elements. The prediction of the equilibrium angle for AH_2 molecules with a Hartree-Fock calculation, until recently, was quite problematical.

Higuchi [7] found a rather slow variation of the energy of NH_2 with angle in the neighborhood of the experimental value and a minimum of 105° , but the integrals were not evaluated in a consistent fashion. The equilibrium angle calculated by Ellison and Shull [8] was considerably greater than the experimental value. Using approximate integrals, Krauss and Padgett [9] determined the molecular geometry of CH_2 which was in poor agreement with experimental results. An accurate configuration interaction calculation by Foster and Boys [10] did not find any better agreement with the experimental equilibrium configuration for either the singlet or triplet ground states of CH_2 . The total energy, however, is in the neighborhood of the expected Hartree-Fock limit. This emphasizes the relative unimportance of correlation in determining the geometry of a molecule.

SCF results, considerably more accurate than those cited above, have recently been published by Moccia [11]. Using a large number of functions in a one-center expansion, he obtained equilibrium configurations that are in good agreement with the experimental value confirming the impression that the correlation of electrons plays a small role in determining the geometry.

Approximate Hartree-Fock orbitals and energies of the same order as those obtained by Moccia can be obtained readily with Gaussian basis sets. Preliminary results for CH_4 and NH_4^+ [12] were quite encouraging. Qualitatively interesting results have been reported by Harrison [13], but the number of basis functions that were used for H_2O were insufficient to yield a quantitative result. Extending the basis slightly, however, produced both a large improvement in the total energy and the calculated equilibrium angle. These results indicate that moderately accurate Gaussian SCF results can predict the structures of radicals and ions. Calculations for H_3 , CH_2 , NH_2 , H_2O , H_2O^+ , BH_4^- , NH_4^+ , and CH_4 will be reported in this paper.

The SCF results also yield enough data to test the contentions of Coulson and Neilson. It will be seen that the simple one-electron picture is unsatisfactory since the partitioned energies reflect the influence of the other orbitals in a complex fashion. Such conclusions must be qualified by observing that accurate Hartree-Fock values have not been obtained but these results provide a consistent test with functions that do predict a moderately accurate geometry.

2. Results of Gaussian Calculations

The SCF calculations follow a standard procedure that has recently been reviewed by Nesbet [4]. Since the open shell is of different symmetry from all other occupied orbitals,

the Nesbet and Roothaan [14] procedures are equivalent and the SCF equations may be solved by the same procedures used for a closed-shell system with a suitably modified A matrix.

For CH_2 , $^3\Sigma_g^-$, which can be represented

$$(1\sigma_g)^2(2\sigma_g)^2(1\sigma_u)^2\Pi_+\Pi_-$$

the eigenvalues are given by the following expressions

$$\begin{aligned}\epsilon_{\alpha\sigma_g} &= E_{\alpha\sigma_g} + J_{\alpha\sigma_g\alpha\sigma_g} + 2J_{1\sigma_g2\sigma_g} - K_{1\sigma_g2\sigma_g} + 2J_{\alpha\sigma_g1\sigma_u} - K_{\alpha\sigma_g1\sigma_u} + 2J_{\alpha\sigma_g\Pi} - K_{\alpha\sigma_g\Pi}, \\ \epsilon_{1\sigma_u} &= E_{1\sigma_u} + J_{1\sigma_u1\sigma_u} + 2J_{1\sigma_u1\sigma_g} - K_{1\sigma_u1\sigma_g} + 2J_{1\sigma_u2\sigma_g} - K_{1\sigma_u2\sigma_g} + 2J_{1\sigma_u\Pi} - K_{1\sigma_u\Pi}, \\ \epsilon_{\Pi_{\pm}} &= E_{\Pi} + \sum_{\alpha} [2J_{\alpha\sigma_g\Pi} - K_{\alpha\sigma_g\Pi}] + 2J_{1\sigma_u\Pi} - K_{1\sigma_u\Pi} + J_{\Pi_+\Pi_-} - K_{\Pi_+\Pi_-},\end{aligned}$$

where E_i is the expectation value for the i th orbital overall one-electron, potential and kinetic energy, operators, J_{ij} is the Coulomb integral between the i and j orbitals, K_{ij} is the exchange integral between these orbitals, and $\alpha=1$ or 2 . The total energy for CH_2 , $^3\Sigma_g^-$, is then

$$E = \sum e_i$$

with

$$e_i = E_i + \epsilon_i.$$

Different expressions are required for H_3 , which is represented by the configuration

$$(1\sigma_g)^2(1\sigma_u).$$

The eigenvalues are

$$\begin{aligned}\epsilon_{1\sigma_g} &= E_{1\sigma_g} + J_{1\sigma_g1\sigma_g} - \frac{1}{2}K_{1\sigma_g1\sigma_u} + J_{1\sigma_g1\sigma_u}, \\ \epsilon_{1\sigma_u} &= E_{1\sigma_u} + 2J_{1\sigma_g1\sigma_u} - K_{1\sigma_g1\sigma_u},\end{aligned}$$

with

$$E = \epsilon_{1\sigma_g} + \frac{1}{2}\epsilon_{1\sigma_u} + E_{1\sigma_g} + \frac{1}{2}E_{1\sigma_u}.$$

A similar result is obtained for NH_2 , 2B_1 , which is represented by the configuration

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^21b_1$$

where

$$\begin{aligned}\epsilon_{\alpha a_1} &= E_{\alpha a_1} + \sum_{\beta} [2J_{\alpha a_1\beta a_1} - K_{\alpha a_1\beta a_1}] + 2J_{\alpha a_11b_2} - K_{\alpha a_11b_2} + J_{\alpha a_11b_1} - \frac{1}{2}K_{\alpha a_11b_1}, \\ \epsilon_{1b_2} &= E_{1b_2} + J_{1b_21b_2} + \sum_{\alpha} [2J_{\alpha a_11b_2} - K_{\alpha a_11b_2}] + J_{1b_11b_2} - \frac{1}{2}K_{1b_11b_2}, \\ \epsilon_{1b_1} &= E_{1b_1} + \sum_{\alpha} [2J_{\alpha a_11b_1} - K_{\alpha a_11b_1}] + 2J_{1b_21b_1} - K_{1b_21b_1},\end{aligned}$$

and

$$E = \sum_{\alpha} \epsilon_{\alpha a_1} + \epsilon_{1b_2} + \frac{1}{2}\epsilon_{1b_1} + \sum_{\alpha} E_{\alpha a_1} + E_{1b_2} + \frac{1}{2}E_{1b_1}.$$

The use of Gaussian basis functions is recommended for polyatomic calculations because of the ease with which the necessary matrix elements are evaluated (15). However, so many functions are required in order to achieve an accurate Hartree-Fock function that in only five cases, CH_4 , NH_4^+ , BH_4^- , $\text{CH}_2(^3\Sigma_g^-)$, and H_3 , was an energy obtained that is sufficiently accurate to warrant an analysis of the energy. For all other cases only the angular variation of the approximate energy was considered.

The parameters for the basis orbitals are given in table 1. The tetrahedral orbital parameters were either scaled from the best H atom results of Longstaff and Singer [16] or were varied in a limited manner to minimize the energy. For H_2O the choice of parameters was

dictated by the desire to compare the present results with those reported by Harrison. The parameters for CH₂ and NH₂ were chosen by reference to various atom results that have been obtained by Huzinaga [17].

In table 2, the eigenvalues, functions and energies for all of the relevant cases are presented. Note that all results are for normalized basis functions. The equilibrium angles and internuclear separations were obtained simply from a quadratic fit and only the three solutions in the neighborhood of the equilibrium are given. Calculated equilibrium angles and distances are compared in table 3 with the experimental values. For the case of BH₄⁻, CH₂(³Σ_g⁻), and H₃ a summary of the considerations relevant to determining a bound on the correlation energy are presented in table 4. Finally we have tabulated the quantities, e_i , for CH₂, NH₂, and H₂O in table 5.

TABLE 1a. Parameters for T_D basis orbitals Nf(x,y,z)exp(-ar²)

Symmetry type	Orbital	f(x,y,z)	Atom			
			H	B	C	N
a ₁ -----	1	1	-----	834.54	1227.4	1695.9
	2	1	-----	128.83	189.48	261.79
	3	1	-----	33.769	49.667	68.623
	4	1	-----	13.873	20.404	28.191
	5	1	-----	5.697	8.379	11.577
	6	1	-----	2.0393	2.999	4.144
	7	r ²	-----	6.08	9.5	13.68
	8	r ²	-----	0.832	1.3	1.87
	9	r ²	-----	.307	0.48	0.69
	10	1	-----	5.74		
1/4(h ₁ +h ₂ +h ₃ +h ₄).-----	11	1	-----	0.775		
	12	1	-----	.159		
t ₁ -----	1	(x,y,z)	-----	9.6	15.0	21.6
	2	(x,y,z)	-----	1.92	3.0	4.32
	3	(x,y,z)	-----	0.448	0.7	1.
	4	(x,y,z)	-----	.128	.2	0.29
[1/4(h ₁ +h ₂ -h ₃ -h ₄), 1/4(h ₁ -h ₂ -h ₃ +h ₄), 1/4(h ₁ -h ₂ +h ₃ -h ₄)]	5	1	-----	5.74		
	6	1	-----	0.775		
	7	1	-----	.159		

TABLE 1b. Parameters for C_{2v} basis orbitals Nf(x,y,z)exp(-ar²)

Symmetry type	Orbital	f(x,y,z)	Atom			
			H	C	N	O
a ₁ -----	1	1	-----	1300	2500	2500
	2	1	-----	575	637.5	1090
	3	1	-----	146	203	276
	4	1	-----	37.3	63.5	70.4
	5	1	-----	9.42	20.2	17.8
	6	1	-----	2.39	6.35	4.51
	7	1	-----	0.608	0.7	1.15
	8	1	-----	.154	.21	0.291
	9	z	-----	4.78	6.89	9.38
	10	z	-----	0.923	1.33	1.81
	11	z	-----	.178	0.257	0.35
	12	1	-----	^a 4.24, 5.74		
	13	1	-----	0.658, 0.775		
	14	1	-----	0.148, 0.159		
b ₂ -----	1	y	-----	4.78	6.89	9.38
	2	y	-----	0.923	1.33	1.81
	3	y	-----	.178	0.257	0.35
	4	1	-----	^a 4.24, 5.74		
1/2(h ₁ -h ₂)-----	5	1	-----	0.658, 0.775		
	6	1	-----	0.148, 0.159		
b ₁ -----	1	x	-----	4.78	6.89	9.38
	2	x	-----	0.923	1.33	1.81
	3	x	-----	.178	0.257	0.35

^a The first column of H parameters were used only for the H₂O calculations.

TABLE 1c. Parameters for D_{∞h} basis orbitals Nf(x, y, z) exp(-ar²)(CH₂)

Symmetry type	Orbital	f(x, y, z)	Atom	
			H	C
1σ _g -----	1	1	-----	4232.61
	2	1	-----	634.882
	3	1	-----	146.097
	4	1	-----	42.4974
	5	1	-----	14.1892
	6	1	-----	5.14773
	7	1	-----	1.96655
	8	1	-----	0.496241
	9	1	-----	.153313
	10	1	-----	5.74
1/2(h ₁ +h ₂)-----	11	1	-----	0.775
	12	1	-----	.159
1σ _u -----	1	z	-----	18.1557
	2	z	-----	3.9864
	3	z	-----	1.14293
	4	z	-----	0.35945
	5	z	-----	.114595
1/2(h ₁ -h ₂)-----	6	1	-----	5.74
	7	1	-----	0.775
	8	1	-----	.159
	1	x	-----	18.1557
	2	x	-----	3.9864
	3	x	-----	1.14293
	4	x	-----	0.35945
	5	x	-----	.114595

TABLE 1d. Parameters for D_{∞h} basis orbitals Nf(x²y, z)exp(-ar²)(H₃)

Symmetry type	Orbital	f(x, y, z)	H
1σ _g -----	1	z	0.8
1/2(p _A -p _B)-----	2	1	22.683
1/2(h _A +h _B)-----	3	1	3.6674
	4	1	0.972
	5	1	.3094
	6	1	.1209
h _c -----	7	1	22.683
	8	1	3.6674
	9	1	0.972
	10	1	.3094
	11	1	.1209
1σ _u -----	1	z	.8
p _c -----	2	z	.8
1/2(p _A +p _B)-----	3	1	22.683
1/2(h _A -h _B)-----	4	1	3.6674
	5	1	0.972
	6	1	.3094
	7	1	.1209

TABLE 2a. BH_4^- Eigenvalues, eigenvector coefficients, and total energy

Internuclear separation (a.u.) ^a	2.1			2.3			2.4		
Total energy (a.u.)	-26.9155			-26.9449			-26.9451		
	$1a_1$	$2a_1$	$1t_2$	$1a_1$	$2a_1$	$1t_2$	$1a_1$	$2a_1$	$1t_2$
Eigenvalue	-7.2087	-0.4625	-0.1789	-7.2676	-0.4434	-0.1765	-7.2974	-0.4347	-0.1755
Eigenvector:									
1.....	.0057	-.0009	.0118	.0057	-.0009	.0109	.0057	-.0009	.0106
2.....	.0398	-.0071	.0848	.0398	-.0067	.0784	.0398	-.0066	.0755
3.....	.1256	-.0198	.2701	.1256	-.0183	.2581	.1257	-.0177	.2523
4.....	.2083	-.0576	.1569	.2088	-.0579	.1581	.2089	-.0583	.1597
5.....	.4266	-.1020	.0980	.4270	-.0966	.0942	.4271	-.0943	.0928
6.....	.3383	.0436	.6087	.3373	.0561	.5887	.3369	.0618	.5783
7.....	.0017	-.0349	.9952	.0022	-.0383	1.0300	.0023	-.0401	1.0459
8.....	.0164	.2252	-----	.0157	.2273	-----	.0154	.2284	-----
9.....	-.0027	.1565	-----	-.0021	.1863	-----	-.0019	.2007	-----
10.....	.0004	.0910	-----	.0002	.0847	-----	.0002	.0816	-----
11.....	.0031	.4946	-----	.0023	.4715	-----	.0020	.4600	-----
12.....	.0026	.6281	-----	.0021	.6586	-----	.0019	.6740	-----

^a Energy in units of $e^2/a_0=27.21$ eV.
Length in units of $a_0=0.52917 \times 10^{-8}$ cm.

TABLE 2b. CH_4 Eigenvalues, eigenvector coefficients, and total energy

Internuclear separation (a.u.)	1.9			2.0665			2.2		
Total energy (a.u.)	-40.1495			-40.1668			-40.1521		
	$1a_1$	$2a_1$	$1t_2$	$1a_1$	$2a_1$	$1t_2$	$1a_1$	$2a_1$	$1t_2$
Eigenvalue	-11.1691	-0.9803	-0.5650	-11.2121	-0.9421	-0.5411	-11.2458	-0.9147	-0.5234
Eigenvector:									
1.....	.0056	-.0010	.0142	.0056	-.0010	.0136	.0056	-.0010	.0131
2.....	.0393	-.0077	.1005	.0393	-.0075	.0966	.0393	-.0075	.0940
3.....	.1247	-.0206	.3378	.1248	-.0195	.3252	.1248	-.0189	.3158
4.....	.2093	-.0729	.2612	.2096	-.0753	.2723	.2098	-.0773	.2803
5.....	.4299	-.1038	.1021	.4302	-.0988	.0966	.4303	-.0958	.0927
6.....	.3341	.0922	.6327	.3334	.1026	.6148	.3330	.1095	.5980
7.....	.0023	-.0478	.5911	.0026	-.0526	.6319	.0028	-.0561	.6670
8.....	.0151	.2871	-----	.0146	.2839	-----	.0142	.2829	-----
9.....	-.0005	.3000	-----	-.0003	.3223	-----	-.0002	.3381	-----
10.....	.0002	.0942	-----	.0002	.0843	-----	.0002	.0770	-----
11.....	.0022	.4549	-----	.0017	.4322	-----	.0013	.4154	-----
12.....	.0004	.3612	-----	.0004	.3964	-----	.0004	.4243	-----

TABLE 2c. NH_4^+ Eigenvalues, eigenvector coefficients, and total energy

Internuclear separation (a.u.)	1.8			1.9464			2.2		
Total energy (a.u.)	-56.4860			-56.5038			-56.4383		
	$1a_1$	$2a_1$	$1t_2$	$1a_1$	$2a_1$	$1t_2$	$1a_1$	$2a_1$	$1t_2$
Eigenvalue	-15.9302	-1.6026	-1.0425	-15.9444	-1.5418	-0.9930	-15.9578	-1.4487	-0.9146
Eigenvector:									
1.....	.0056	-.0011	.0161	.0056	-.0011	.0155	.0056	-.0011	.0149
2.....	.0389	-.0083	.1189	.0389	-.0082	.1171	.0389	-.0083	.1145
3.....	.1242	-.0212	.3815	.1243	-.0205	.3680	.1243	-.0198	.3483
4.....	.2094	-.0882	.3439	.2096	-.0917	.3621	.2098	-.0963	.3844
5.....	.4327	-.1005	.1045	.4329	-.0961	.0968	.4330	-.0922	.0848
6.....	.3317	.1241	.5706	.3313	.1330	.5528	.3308	.1445	.5214
7.....	.0021	-.0605	.3198	.0023	-.0656	.3637	.0025	-.0719	.4488
8.....	.0140	.3177	-----	.0136	.3158	-----	.0132	.3177	-----
9.....	.0007	.3963	-----	.0008	.4147	-----	.0008	.4409	-----
10.....	.0002	.0874	-----	.0002	.0756	-----	.0002	.0606	-----
11.....	.0011	.3980	-----	.0009	.3810	-----	.0006	.3501	-----
12.....	-.0001	.2349	-----	-.0000	.2636	-----	.0001	.3113	-----

TABLE 2d. CH₂, ¹A₁, *Eigenvalues, eigenvector coefficients, and total energy*

Internuclear separation	100°				105°				110°			
$R_{CH}=2.1$ (a.u.) Total energy (a.u.)	-38.8017				-38.8026				-38.8020			
	1a ₁	2a ₁	3a ₁	1b ₂	1a ₁	2a ₁	3a ₁	1b ₂	1a ₁	2a ₁	3a ₁	1b ₂
Eigenvalue.....	-11.3144	-0.9145	-0.3934	-0.5623	-11.3120	-0.9095	-0.3859	-0.5712	-11.3095	-0.9047	-0.3784	-0.5793
Eigenvector:												
1.....	.0036	-.0006	.0003	.0637	.0036	-.0006	.0003	.0635	.0036	-.0006	.0003	.0634
2.....	.0062	-.0011	.0005	.3324	.0062	-.0011	.0005	.3319	.0062	-.0011	.0005	.3317
3.....	.0477	-.0088	.0047	.3119	.0477	-.0088	.0045	.3092	.0477	-.0089	.0044	.3081
4.....	.2098	-.0398	.0209	.0663	.2098	-.0400	.0202	.0667	.2098	-.0402	.0194	.0672
5.....	.5740	-.1394	.0766	.5181	.5739	-.1401	.0738	.5190	.5739	-.1408	.0710	.5187
6.....	.3339	-.1577	.0817	.4027	.3339	-.1586	.0789	.3860	.3339	-.1595	.0759	.3699
7.....	-.0308	.4535	-.2430	-----	-.0308	.4561	-.2350	-----	-.0307	.4586	-.2265	-----
8.....	.0209	.4495	-.4530	-----	.0209	.4505	-.4361	-----	.0208	.4502	-.4196	-----
9.....	.0027	.0192	.0739	-----	.0027	.0183	.0749	-----	.0027	.0175	.0759	-----
10.....	-.0003	.1183	.3578	-----	-.0002	.1137	.3621	-----	-.0002	.1089	.3663	-----
11.....	.0040	.1232	.4993	-----	.0038	.1176	.5157	-----	.0035	.1115	.5316	-----
12.....	-.0006	.0536	.0331	-----	-.0006	.0531	.0323	-----	-.0006	.0525	.0313	-----
13.....	.0047	.3453	.2279	-----	.0049	.3439	.2209	-----	.0050	.3432	.2138	-----
14.....	-.0137	.0560	.2391	-----	-.0137	.0600	.2314	-----	-.0136	.0652	.2245	-----

TABLE 2e. CH₂, ³Σ_g⁻, *Eigenvalues, eigenvector coefficients, and total energy*

Internuclear separation (a.u.)	1.8				1.95				2.1			
Total energy (a.u.)	-38.8731				-38.8936				-38.8915			
	1σ _g	2σ _g	1σ _u	π	1σ _g	2σ _g	1σ _u	π	1σ _g	2σ _g	1σ _u	π
Eigen value.....	-11.2185	-0.8915	-0.6886	-0.3973	-11.2326	-0.8635	-0.6520	-0.3944	-11.2456	-0.8371	-0.6183	-0.3920
Eigen vector:												
1.....	.0012	-.0002	.0117	.0136	.0012	-.0002	.0109	.0136	.0012	-.0002	.0102	.0136
2.....	.0093	-.0018	.0652	.0841	.0093	-.0018	.0631	.0845	.0093	-.0017	.0609	.0849
3.....	.0454	-.0087	.2322	.2755	.0454	-.0086	.2145	.2751	.0454	-.0085	.1998	.2759
4.....	.1544	-.0320	.3368	.5001	.1545	-.0312	.3472	.4954	.1545	-.0307	.3501	.4910
5.....	.3583	-.0805	.0592	.3617	.3584	-.0795	.0628	.3676	.3584	-.0786	.0697	.3721
6.....	.4365	-.1515	.0835	-----	.4368	-.1472	.0771	-----	.4371	-.1447	.0718	-----
7.....	.1478	-.0562	.4379	-----	.1473	-.0582	.4261	-----	.1469	-.0592	.4177	-----
8.....	.0032	.4975	.3200	-----	.0031	.4974	.3560	-----	.0030	.4947	.3899	-----
9.....	.0006	.2893	-----	-----	.0005	.3127	-----	-----	.0005	.3368	-----	-----
10.....	.0003	.0590	-----	-----	.0002	.0534	-----	-----	.0001	.0487	-----	-----
11.....	.0014	.3746	-----	-----	.0011	.3563	-----	-----	.0009	.3369	-----	-----
12.....	-.0005	.1620	-----	-----	-.0004	.1735	-----	-----	-.0003	.1852	-----	-----

TABLE 2f. NH₂, ²B₁, *Eigenvalues, eigenvector coefficients, and total energy*

Internuclear separation	95°					105°					115°				
$R_{NH}=1.95$ (a.u.) Total energy (a.u.)	-55.4496					-55.4537					-55.4523				
	1a ₁	2a ₁	3a ₁	1b ₂	1b ₁	1a ₁	2a ₁	3a ₁	1b ₂	1b ₁	1a ₁	2a ₁	3a ₁	1b ₂	1b ₁
Eigenvalue.....	-15.6019	-1.1341	-0.4892	-0.6149	-0.5049	-15.5953	-1.1230	-0.4709	-0.6332	-0.5005	-15.5879	-1.1128	-0.4531	-0.6486	-0.4957
Eigenvector:															
1.....	.0029	-.0005	.0003	.0694	.0965	.0029	-.0006	.0002	.0687	.0962	.0029	-.0006	.0002	.0682	.0959
2.....	.0096	-.0018	.0008	.3417	.4640	.0096	-.0019	.0008	.3387	.4622	.0096	-.0019	.0007	.3368	.4603
3.....	.0385	-.0077	.0036	.3854	.6611	.0385	-.0077	.0033	.3783	.6628	.0385	-.0078	.0031	.3762	.6647
4.....	.1452	-.0295	.0133	.0674	-----	.1452	-.0297	.0123	.0688	-----	.1452	-.0299	.0113	.0699	-----
5.....	.3752	-.0892	.0423	.4941	-----	.3752	-.0899	.0392	.4968	-----	.3752	-.0904	.0360	.4941	-----
6.....	.5361	-.1829	.0841	.3237	-----	.5360	-.1843	.0780	.2938	-----	.5360	-.1855	.0717	.2686	-----
7.....	.0737	.4764	-.2295	-----	.0740	.4799	-.2140	-----	.0742	.4830	-.1969	-----	-----	-----	-----
8.....	-.0416	.4438	-.3721	-----	-.0422	.4479	-.3473	-----	-.0424	.4488	-.3240	-----	-----	-----	-----
9.....	.0018	.0164	.0777	-----	.0018	.0150	.0799	-----	.0018	.0135	.0819	-----	-----	-----	-----
10.....	.0025	.0966	.3626	-----	.0023	.0888	.3717	-----	.0021	.0808	.3805	-----	-----	-----	-----
11.....	-.0067	.1126	.5052	-----	-.0062	.1035	.5331	-----	-.0054	.0930	.5593	-----	-----	-----	-----
12.....	.0011	.0507	.0413	-----	.0011	.0496	.0393	-----	.0012	.0486	.0367	-----	-----	-----	-----
13.....	-.0027	.2790	.2625	-----	-.0032	.2756	.2428	-----	-.0039	.2756	.2245	-----	-----	-----	-----
14.....	.0207	.0223	.2239	-----	.0215	.0249	.2169	-----	.0221	.0294	.2100	-----	-----	-----	-----

TABLE 2g. H_2O , $^1\text{A}_1$, *Eigenvalues, eigenvector coefficients, and total energy*

Inter-nuclear separation	95°					105°					110°				
$R_{\text{OH}} = 1.8$ (a.u.) Total energy (a.u.)	-75.8384					-75.8453					-75.8450				
	$1a_1$	$2a_1$	$3a_1$	$1b_2$	$1b_1$	$1a_1$	$2a_1$	$3a_1$	$1b_2$	$1b_1$	$1a_1$	$2a_1$	$3a_1$	$1b_2$	$1b_1$
Eigenvalue	-20.5836	-1.3816	-0.5794	-0.6879	-0.5048	-20.5757	-1.3697	-0.5591	-0.7061	-0.4996	-20.5709	-1.3638	-0.5490	-0.7141	-0.4967
Eigenvector:															
1	.0033	-.0007	.0003	.0755	.1002	.0033	-.0007	.0003	.0745	.0999	.0033	-.0007	.0002	.0741	.0998
2	.0059	-.0011	.0004	.3555	.4529	.0059	-.0011	.0004	.3517	.4515	.0059	-.0011	.0004	.3501	.4507
3	.0451	-.0095	.0038	.4205	.6696	.0451	-.0095	.0035	.4122	.6710	.0451	-.0096	.0034	.4097	.6718
4	.2016	-.0433	.0169	.0954	-----	.2016	-.0436	.0156	.0982	-----	.2016	-.0437	.0149	.0993	-----
5	.5711	-.1601	.0654	.4760	-----	.5711	-.1611	.0604	.4759	-----	.5711	-.1614	.0578	.4740	-----
6	.3461	-.1675	.0626	.2426	-----	.3461	-.1685	.0579	.2189	-----	.3461	-.1689	.0554	.2092	-----
7	-.0303	.4886	-.2007	-----	-----	-.0303	.4912	-.1862	-----	-----	-.0303	.4923	-.1785	-----	-----
8	.0184	.5440	-.3502	-----	-----	.0185	.5476	-.3241	-----	-----	.0186	.5487	-.3116	-----	-----
9	.0021	.0145	.0831	-----	-----	.0020	.0132	.0854	-----	-----	.0019	.0125	.0865	-----	-----
10	-.0000 ₁	.0820	.3761	-----	-----	.0000 ₁	.0752	.3856	-----	-----	.0000 ₂	.0716	.3901	-----	-----
11	.0026	.1050	.5205	-----	-----	.0023	.0957	.5472	-----	-----	.0021	.0905	.5594	-----	-----
12	-.0005	.0692	.0627	-----	-----	-.0005	.0676	.0593	-----	-----	-.0006	.0669	.0573	-----	-----
13	-.0010	.2099	.2769	-----	-----	-.0006	.2091	.2491	-----	-----	-.0004	.2100	.2371	-----	-----
14	-.0068	-.0138	.1693	-----	-----	-.0072	-.0131	.1668	-----	-----	-.0073	.0127	.1650	-----	-----

TABLE 2h. H_2O^+ , $^2\text{B}_1$: *Eigenvalues, eigenvector coefficients, and total energy*

Inter-nuclear separation	105°					115°					125°				
$R_{\text{OH}} = 1.9$ (a.u.) Total energy (a.u.)	-75.4427					-75.4465					-75.4462				
	$1a_1$	$2a_1$	$3a_1$	$1b_2$	$1b_1$	$1a_1$	$2a_1$	$3a_1$	$1b_2$	$1b_1$	$1a_1$	$2a_1$	$3a_1$	$1b_2$	$1b_1$
Eigenvalue	-21.1628	-1.8434	-1.0539	-1.1732	-1.1154	-21.1536	-1.8323	-1.0372	-1.1859	-1.1096	-21.1437	-1.8214	-1.0211	-1.1964	-1.1032
Eigenvector:															
1	.0033	-.0007	.0002	.0841	.1080	.0033	-.0007	.0002	.0832	.1077	.0033	-.0007	.0002	.0825	.1074
2	.0059	-.0012	.0004	.4009	.5135	.0059	-.0012	.0003	.3964	.5119	.0059	-.0012	.0003	.3925	.5102
3	.0451	-.0100	.0033	.4721	.6087	.0451	-.0100	.0029	.4720	.6103	.0451	-.0100	.0026	.4754	.6122
4	.2016	-.0456	.0149	.0607	-----	.2016	-.0458	.0134	.0624	-----	.2016	-.0460	.0119	.0639	-----
5	.5713	-.1686	.0563	.4126	-----	.5713	-.1693	.0508	.4067	-----	.5713	-.1699	.0449	.3965	-----
6	.3460	-.1781	.0594	.0951	-----	.3460	-.1790	.0537	.0850	-----	.3461	-.1799	.0475	.0762	-----
7	-.0303	.5395	-.2030	-----	-----	-.0303	.5424	-.1837	-----	-----	-.0303	.5449	-.1625	-----	-----
8	.0177	.5581	-.2063	-----	-----	.0178	.5597	-.1866	-----	-----	.0179	.5604	-.1665	-----	-----
9	.0019	.0139	.0939	-----	-----	.0018	.0125	.0960	-----	-----	.0017	.0109	.0980	-----	-----
10	-.0000 ₄	.0775	.4339	-----	-----	-.0000 ₂	.0701	.4435	-----	-----	.0000 ₁	.0620	.4527	-----	-----
11	.0022	.1084	.5537	-----	-----	.0019	.0962	.5699	-----	-----	.0016	.0832	.5849	-----	-----
12	-.0007	.0409	.0382	-----	-----	-.0007	.0398	.3500	-----	-----	-.0008	.0388	.6312	-----	-----
13	-.0002	.1890	.2065	-----	-----	.0002	.1912	.1867	-----	-----	.0005	.1947	.1667	-----	-----
14	-.0070	-.0438	.0909	-----	-----	-.0073	-.0437	.0843	-----	-----	-.0075	.0430	.0769	-----	-----

TABLE 2i. H_3 , $^2\Sigma_u^+$: *Eigenvalues, eigenvector coefficients, and total energy*

Internuclear separation (a.u.)	1.5		1.6		1.7		1.8		1.9	
Total energy (a. u.)	-1.58123		-1.58975		-1.59296		-1.59215		-1.58829	
	$1\sigma_g$	$1\sigma_u$	$1\sigma_g$	$1\sigma_u$	$1\sigma_g$	$1\sigma_u$	$1\sigma_g$	$1\sigma_u$	$1\sigma_g$	$1\sigma_u$
Eigenvalue	-.70835	-0.36524	-0.67876	-0.37499	-0.65241	-0.38284	-0.62878	-0.38910	-0.60745	-0.39403
Eigenvector:										
1	-.04341	.05451	-.04188	.04980	-.04055	.04621	-.03938	.04344	-.03831	.04128
2	.01194	.01112	.01153	.00482	.01117	-.00029	.01085	-.00451	.01056	-.00804
3	.06917	.01508	.06607	.01494	.06344	.01478	.06119	.01461	.05928	.01445
4	.24285	.09069	.23591	.08995	.22943	.08913	.22333	.08823	.21755	.08725
5	.32236	.32523	.32278	.32481	.32360	.32275	.32468	.31985	.32582	.31658
6	.12731	.62984	.14340	.62627	.15885	.62148	.17377	.61579	.18825	.60939
7	.00861	.90347	.00829	.84821	.00801	.80637	.00775	.77481	.00752	.75126
8	.05011	-----	.04812	-----	.04643	-----	.04492	-----	.04353	-----
9	.17421	-----	.16811	-----	.16253	-----	.15750	-----	.15299	-----
10	.24290	-----	.24758	-----	.25009	-----	.25088	-----	.25039	-----
11	.11472	-----	.12665	-----	.13898	-----	.15150	-----	.16406	-----

TABLE 3. Summary of results

	$R_e(\text{a.u.})$		$E_e(\text{a.u.})$
	Calculated	Experimental	
BH_4^- -----	2.35	^a 2.37	-26.946
CH_4 -----	2.05	^b 2.062	-40.167
NH_4^+ -----	1.94	^c 1.95	-56.504
$\text{CH}_2, {}^3\Sigma^-_g$ -----	2.01	^d 1.95	-38.889
H_3 -----	1.73	-----	-1.593
	R	θ_e	
$\text{CH}_2, {}^1\text{A}_1$ -----	2.1	Calculated 105°27'	^d 103°
NH_2 -----	1.95	107°29'	^e 103°23'
H_2O -----	1.8	106°56'	^f 104°27'
H_2O^+ -----	1.9	119°23'	-----

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TABLE 4. Deduction of bound to correlation energy (a.u.)

	BH_4^-	$\text{CH}_2, {}^3\Sigma^-_g$	H_3
Calculated Hartree-Fock approximation-----	-26.946	-38.895	-1.593
Heat of atomization-----	^a - .550	^b - .283	^c - .154, ^f - .151
Zero point energy-----	^a - .034	- .02	^d - .009
Energy of separated atoms--	-26.680	-38.855	-1.5
Relativistic correction-----	^e - .005	^e - .012	
Hartree-Fock energy for separated atoms-----	-26.529	-38.689	-1.499
Hartree-Fock heat of atomization+zero-point energy-----	- .417	- .200	- .094
Upper limit to molecular correlation energy-----	- .319	- .28	- .070, - .067

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TABLE 5. Partition of molecular energy, -e_i

Orbital	1a ₁	2a ₁	3a ₁	1b ₂	1b ₁
$\text{H}_2\text{O}, R=1.7$					
105°-----	53.6388	9.3362	7.5375	7.4739	7.6305
115°-----	53.6302	9.3115	7.5286	7.5075	7.6183
125°-----	53.6209	9.2866	7.5233	7.5389	7.6050
135°-----	53.6111	9.2623	7.5231	7.5669	7.5910
$\text{H}_2\text{O}, R=1.8$					
95°-----	53.5918	9.2388	7.4249	7.2463	7.6022
105°-----	53.5838	9.2185	7.4223	7.2693	7.5904
115°-----	53.5742	9.1965	7.4209	7.2940	7.5767
125°-----	53.5638	9.1734	7.4241	7.3178	7.5618
135°-----	53.5525	9.1501	7.4329	7.3391	7.5455
150°-----	53.5351	9.1162	7.4559	7.3642	7.5205
$\text{H}_2\text{O}, R=2$					
105°-----	53.4903	9.0432	7.1825	6.9110	7.5232
115°-----	53.4797	9.0243	7.1972	6.9198	7.5080
125°-----	53.4674	9.0030	7.2169	6.9295	7.4905
135°-----	53.4531	8.9792	7.2449	6.9373	7.4702
150°-----	53.4299	8.9413	7.3034	6.9435	7.4369
$\text{NH}_2, R=1.95$					
95°-----	41.0537	7.2882	5.8303	5.7860	6.0372
105°-----	41.0469	7.2651	5.8117	5.8195	6.0264
115°-----	41.0395	7.2420	5.7955	5.8515	6.0146
$\text{CH}_2, R=2.1$					
90°-----	30.1910	5.6279	4.4646	4.5631	
100°-----	30.1860	5.5980	4.4390	4.6038	
105°-----	30.1836	5.5837	4.4267	4.6229	
110°-----	30.1810	5.5700	4.4148	4.6412	

3. Discussion

It is evident that the approximate Gaussian calculations are adequate for the determination of the molecular geometries of first-row hydrides. The greatest discrepancy between the calculated and experimental equilibrium angles is about 5° and the largest error in the equilibrium internuclear separation is 0.05 a.u. This accuracy is of the order of that reported in reference 5, although a more accurate SCF result for H_2O presented by Moccia yields slightly better agreement between the calculated and experimental angle.

The success of the numerical experimentation permits confidence to be placed in the predicted angle for H_2O^+ , a rather large 119°. This value is totally unexpected from the presumed nonbonding character of the $1b_1$ orbital. Experimental evidence is ambiguous. The

first Rydberg excited state of H_2O has been analyzed (18). Only a small change in angle was observed but it was accompanied by an appreciable increase in the O-H distance. It is usually assumed that the first member of an np Rydberg series does not penetrate the core and influence the bonding, but this is not certain.

From Koopman's theorem the vertical ionization potential for H_2O , 0.465 a.u., is approximated by the orbital energy 0.500 a.u. However, as noted by Clementi (19), the ionization potential is given by

$$I = -\epsilon - E_{RE}^+ + (E_c - E_c^+) + (E_R - E_R^+) + E_{\text{vert}},$$

where E_{RE}^+ is the reorganization energy in computing the SCF energy of the ion, $(E_e - E_e^+)$ is the difference in correlation energies between the neutral and ionic species, $(E_R - E_R^+)$ is the difference in relativistic energies between the neutral and ionic species, and E_{vert} is the internal energy of the ion attendant upon a vertical transition.

$(E_R - E_R^+)$ is very close to zero and for our purposes we shall assume that E_{vert} is also small enough to be neglected. Then the change in correlation energy can be determined from E_{RE}^+ , which is approximately -0.100 a.u., to be about -0.065 a.u. This result is in good agreement with Clementi's [20] estimate of -0.074 a.u. for the correlation energy of a pair. In fact, if we use a better estimate of the CH_4 correlation energy [21], the correlation energy per bonding pair in CH_4 is about -0.067 a.u. or less. The fortuitous cancellation of the reorganization energy and the change in correlation energy is the basis for the success of the application of Koopman's theorem to the prediction of ionization potentials.

The results for H_2O were obtained with SCF calculations some 2 eV higher than those reported by Moccia and some 6.5 eV from the Hartree-Fock limit estimated by Moccia. Agreement of estimated and computed pair correlation energies must be considered in this light.

The results for H_3 are the most accurate of all those reported. The asymptotic error for three H atoms computed with a five S -type Gaussian basis is 0.02 eV and the error in the molecule is probably less than 0.05 eV. Addition of another p -type Gaussian improved the total molecular energy by less than 0.01 eV.

Unfortunately, the Hartree-Fock H_3 surface is of little value for understanding the kinetics of the $\text{H} + \text{H}_2$ system since a radical reaction is primarily a correlation problem. There are also complications due to the inaccurate asymptotic behavior of the molecular orbitals. An estimate of the correlation energy cannot be made from the isoelectronic atoms; the intershell correlation is much larger in H_3 than in Li due to the appreciable differential overlap in the molecule.

The results for BH_4^- are analogous to those reported for CH_4 and NH_4^+ and little can be added to the discussion of BH_4^- . It should be noted, though, that the experimental heat of atomization is not accurately known and there is a corresponding uncertainty in the bound for the molecular correlation energy.

Evidently, the accuracy for the $^3\Sigma_g^-$ state of CH_2 is not comparable to that for the tetrahedral molecules or H_3 . This is evidenced by the large correlation energy limit in table 4. Although the heat of atomization reported for CH_2 may still be too high, the calculated internuclear separation indicates the SCF result for CH_2 is still appreciably above the Hartree-Fock limit. For strongly bonded molecules, it would be expected that most excited configurations required to represent the exact function would have larger equilibrium internuclear separations. The Hartree-Fock equilibrium internuclear separation, therefore, should be smaller than the experimental value. The inadequacy of the Gaussian basis for CH_2 can be attributed to two main defects: (1) no variation of the orbital exponents was attempted, and (2) p -type functions are required on the H atoms.

The final comment is in many ways the most important. A comparison of table 5 with the similar data presented by Coulson and Neilson shows how ill-founded was their expectation that improved molecular wavefunctions would not change their results qualitatively. The behavior of e_{3a1} in the neighborhood of 105° is not at all similar to that exhibited by the curve for 3_{a1} in figure 3 of reference 3. There is little point in examining the differences in detail;

we only need to note that the partitioned energies e_i reflect the influence of the other orbitals in such a way as to render a simple interpretation of these quantities very difficult. The most striking evidence of this effect is the large variation in the e_{1a1} and e_{1b1} even though these molecular orbitals vary only slightly with angle. There is little support for a one-electron type partition of the total energy from the present results.

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